CERTIFICATION

I, Tokihiro MOTOYAMA, c/o ITOH & CO. located at
nomon Denki Bldg., 8-1, Toranomon 2-chome, Minato-ku, Tokyo,
I, hereby certify that I am the translator of the
panying certified official copy of the documents in respect
application for a patent filed in Japan on December 28,
nd of the official certificate attached thereto, and
that the following is a true and correct translation to
t of my knowledge and belief.

T. Motoyama

Tokihiro MOTOYAMA

Dated this 12th day of November

T. Motoyama

PATENT OFFICE

JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Application Number : (Hei.) 1-341245

Applicant(s) : NIPPON OIL CO., LTD.

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Commissioner,

Patent Office Satoshi UEMATSU

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PETITION FOR PATENT 2

December 28, 1989

To Commissioner of the Patent Office

Fumitake YOSHIDA

1. Title of the Invention:

   REFRIGERATOR OILS FOR USE WITH CHLORINE-FREE TYPE HALOGENOCARBON REFRIGERANTS

2. Number of claims 6

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6. List of Attached Documents:

(1) Specification	1 copy
(2) Duplicate of the Petition	1 copy
(3) Power of Attorney	1 copy (This will be filed later.)

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SPECIFICATION

1. Title of the Invention:

REFRIGERATOR OILS FOR USE WITH CHLORINE-FREE TYPE HALOGENOCARBON REFRIGERANTS

2. What is claimed is:

1. A refrigerator oil for use in compressors using therein a chlorine-free type halogenocarbon as a refrigerant, comprising as a major component an ester represented by the general formula

$$X \left[\underset{\underset{O}{\|}}{C} \left(R_1 \right)_{\ell} \underset{\underset{O}{\|}}{C} - O - R_2 - O \right]_n Y$$

wherein X is a group represented by the general formula $-OR_3$ or $-O-R_4-O-\underset{\underset{O}{\|}}{C}-R_5$, Y is a group represented by the general formula $-\underset{\underset{O}{\|}}{C}-R_6$ or $-\underset{\underset{O}{\|}}{C}\left(R_7 \right)_m \underset{\underset{O}{\|}}{C}-OR_8$, R_1 and R_7 are each a divalent hydrocarbon group having 1-8 carbon atoms, R_2 and R_4 are each a divalent saturated hydrocarbon group having 2-16 carbon atoms, R_3 and R_8 are each an alkyl group having 1-15 carbon atoms, R_5 and R_6 are

each an alkyl group having 1-14 carbon atoms, l and m are each an integer of 0 or 1 and n is an integer of 0-30.

2. A refrigerator oil according to claim 1, wherein the ester is comprised as a base oil.

3. A refrigerator oil according to claim 1, comprising as a base oil a mixture oil of:

(I) the ester, and

(II) at least one kind of an oil selected from the group consisting of

a polyoxyalkylene glycol or an ether thereof represented by the general formula

$$R_9 - (OR_{11})_a - OR_{10}$$

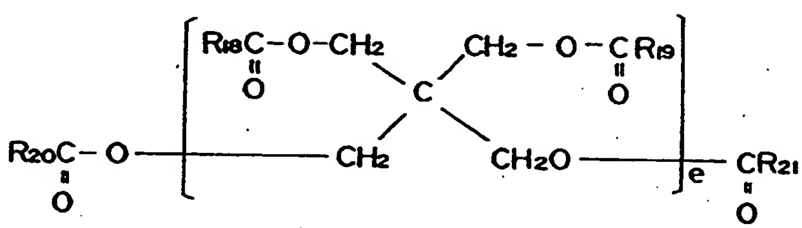
wherein R_9 and R_{10} are each a hydrogen atom or an alkyl group having 1-18 carbon atoms, R_{11} is an alkylene group having 2-4 carbon atoms, and a is an integer of 5-70,

a polyoxyalkylene glycol glycerol ether represented by the general formula

$$\begin{array}{l} H_2C - O - (R_{15}O)_b - R_{12} \\ \quad | \\ HC - O - (R_{16}O)_c - R_{13} \\ \quad | \\ H_2C - O - (R_{17}O)_d - R_{14} \end{array}$$

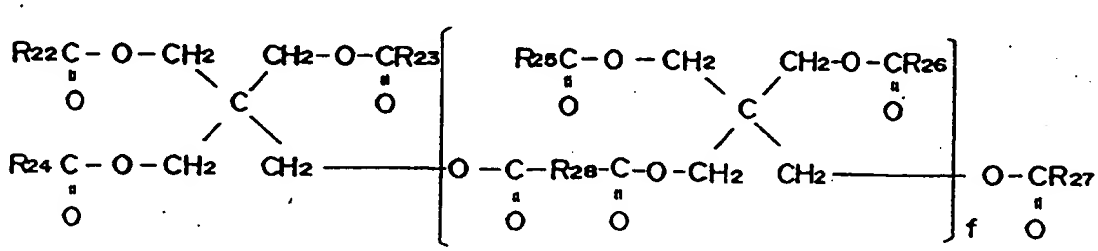
wherein R_{12}-R_{14} are each a hydrogen atom or an alkyl group having 1-18 carbon atoms, R_{15} -R_{17} are each an alkylene group having 2-4 carbon atoms, and b-d are each an integer of 5-7,

a pentaerythritol ester represented by the general formula



wherein R_{18}-R_{21} may be identical with, or different from, each other and are each a group selected from the group consisting of straight-chain alkyl groups having 3-11 carbon atoms, branched-chain alkyl groups having 3-15 carbon atoms and cycloalkyl groups having 6-12 carbon atoms, the straight-chain alkyl groups being present in a ratio of not more than 60 % of the total alkyl groups, and e is an integer of 1-3, and

a pentaerythritol dicarboxylic acid ester represented by the general formula



wherein R_{22} - R_{27} are each an alkyl group having 3-15 carbon atoms, R_{28} is a divalent hydrocarbon group having 1-8 carbon atoms and f is an integer of 1-5.

4. A refrigerator oil according to claim 3, wherein the ester (I) is comprised in an amount of more than 50 % by weight based on the total amount of the refrigerator oil.

5. A refrigerator oil according to any one of claims 1-4, further comprising at least one kind of a phosphorous compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters and phosphorous esters, in an amount of 0.1-5.0 % by weight based on the total amount of the refrigerator oil.

6. A refrigerator oil according to any one of claims 1-5, further comprising at least one kind of an epoxy compound selected from the group consisting of phenylglycidyl ether type epoxy compounds, glycidyl ester type epoxy compounds, epoxidized fatty acid monoesters and epoxidized vegetable oils, in an amount of 0.1-5.0 % by weight based on the total amount of the refrigerator oil.

3. Detailed description of the Invention:

[Field of the Invention]

This invention relates to a lubricating oil for compressors of refrigerators using therein a chlorine-free type halogenocarbon as a refrigerant (the oil being hereinafter referred to as "a refrigerator oil for use with a chlorine-free type halogenocarbon refrigerant") and, more specifically, it relates to such a refrigerator oil which comprises an ester having a specific chemical structure as a major component and is superior in various properties.

[Prior Art and Problems to be solved by the Invention]

Generally, naphthenic mineral oils, paraffinic mineral oils, alkylbenzenes, polyglycolic oils, ester oils and mixtures thereof, which have each a kinematic viscosity of 10 - 200 cSt at 40°C, as well as said oils incorporated with suitable additives have been used as refrigerator oils.

On the other hand, chlorofluorocarbons (CFCS) type refrigerants, such as CFC-11, CFC-12, CFC-113 and HCFC-22, have been used for refrigerators.

Of these CFCS, CFCS such as CFC-11, CFC-12 and CFC-113, which are obtained by substituting all the hydrogen atoms of hydrocarbons thereof by halogen atoms including chlorine atoms, may lead to the destruction of the ozone layer, and therefore, the use of the CFCS has been controlled. Accordingly, chlorine-free type halogenocarbons, such as HFC-134a and HFC-152a, have been being used as substitutes for CFCs. HFC-134a is especially hopeful as a substitute refrigerant since it is similar in

thermodynamic properties to CFC-12 which has heretofore been used in many kinds of refrigerators of home cold-storage chests, air-conditioners and the like.

Refrigerator oils require various properties, among which their compatibility with refrigerants is extremely important in regard to lubricity and system efficiency in refrigerators. However, conventional refrigerator oils comprising, as the base oils, naphthenic oils, paraffinic oils, alkylbenzenes, heretofore known ester oils and the like, are hardly compatible with chlorine-free type halogenocarbons such as HFC-134a. Therefore, if said conventional refrigerator oils are used in combination with HFC-134a, the resulting mixture will separate into two layers at normal temperature thereby to degrade the oil-returnability which is the most important within the refrigeration system and cause various troubles such as a decrease in refrigeration efficiency, the deterioration of lubricity and the consequent seizure of the compressor within the system whereby the refrigerator oils are made unsuitable for use as such. In addition, polyglycolic oils are also known as refrigerator oils for their high viscosity index and are disclosed in, for example, Japanese Pat. Gazettes Nos. Sho. 57-42119 and Sho. 61-52880 and Japanese Pat. Appln. Laid-Open Gazette No. Sho. 57-51795. However, the polyglycolic oils concretely disclosed in these prior art publications are not fully compatible with HFC-134a

thereby raising the same problems as above and rendering them unusable.

Further, U.S. Patent No. 4,755,316 discloses polyglycolic refrigerator oils which are compatible with HFC-134a. In addition, the present inventors developed polyglycolic refrigerator oils which have excellent compatibility with HFC-134a as compared with conventional known refrigerator oils, and filed applications for patents for the thus developed polyglycolic refrigerator oils (Japanese Pat. Appln. Laid-Open Gazettes Nos. hei. 1-256594 and hei. 1-271491). It has been found, however, that the polyglycolic oils raise problems as to their high compatibility with water and inferior electrical insulating property.

On the other hand, refrigerator oils used in compressors of home refrigerators and the like are required to have a high electrical insulating property. Among the known refrigerator oils, alkylbenzenes and the mineral oils have the highest insulating property, but they are hardly compatible with chlorine-free type halogenocarbons such as HFC-134a as mentioned above. Therefore, there had been developed no refrigerator oils having both high compatibility with chlorine-free type halogenocarbons such as HFC-134a and a high insulating property before the accomplishment of the present invention.

The present inventors made various intensive studies in attempts to develop refrigerator oils which can meet the

aforesaid requirements and, as the result of their studies, they found that esters having specific structures have excellent compatibility with chlorine-free type halogenocarbons such as HFC-134a, and a high electrical insulating property as well as excellent lubricity. This invention is based on this finding.

The object of this invention is to provide lubricating oils for use with chlorine-free type halogenocarbons refrigerants, the oils comprising as a major component (or a base oil) an ester having a specific structure and having excellent compatibility with chlorine-free type halogenocarbons such as HFC-134a, and a high electrical insulating property.

[Means of Solution to the Problems]

The refrigerator oil of the present invention is characterized in that it comprises as a major component an ester represented by the general formula

$$X\left[\underset{\substack{\|\\O}}{C}-(R_1)_\ell-\underset{\substack{\|\\O}}{C}-O-R_2-O\right]_n Y$$

wherein X is a group represented by the general formula $-OR_3$ or $-O-R_4-O-\underset{\substack{\|\\O}}{C}-R_5$, Y is a group represented by the general formula $-\underset{\substack{\|\\O}}{C}-R_6$ or $-\underset{\substack{\|\\O}}{C}-(R_7)_m-\underset{\substack{\|\\O}}{C}-OR_8$, R_1 and R_7 are each a divalent saturated hydrocarbon group having 1-8

carbon atoms, R_2 and R_4 are each a divalent saturated hydrocarbon group having 2-16 carbon atoms; R_3 and R_8 are each an alkyl group having 1-15 carbon atoms, R_5 and R_6 are each an alkyl group having 1-14 carbon atoms, l and m are each an integer of 0 or 1 and n is an integer of 0-30.

This invention will be explained in more detail hereunder.

The refrigerator oils of the present invention are those comprising as a major component an ester represented by the general formula

$$X \left[\underset{\underset{O}{\|}}{C} \left(R_1 \right)_{\ell} \underset{\underset{O}{\|}}{C} - O - R_2 - O \right]_n Y$$

In the formula, X is a group represented by the general formula $-OR_3$ or $-O-R_4-O-\underset{\underset{O}{\|}}{C}-R_5$, and Y is a group represented by the general formula $-\underset{\underset{O}{\|}}{C}-R_6$ or $-\underset{\underset{O}{\|}}{C}\left(R_7 \right)_m \underset{\underset{O}{\|}}{C}-OR_8$. In addition, R_1 and R_7 are each a divalent hydrocarbon group having 1-8 carbon atoms, preferably 1-6 carbon atoms, R_2 and R_4 are each a divalent saturated hydrocarbon group having 2-16 carbon atoms, preferably 2-9 carbon atoms, R_3 and R_8 are each an alkyl group having 1-15 carbon atoms, preferably 1-12 carbon atoms, and R_5 and R_6 are each an alkyl group having 1-14

carbon atoms, preferably 1-11 carbon atoms. Further, l and m are each an integer of 0 or 1 and n is an integer of 0-30, preferably 1-30. A refrigerator oil comprising as a major component an ester which does not satisfy the above conditions is undesirably inferior in miscibility with a hydrogen-containing halogenocarbon.

R_1 and R_7 are each exemplified by a methylene group, ethylene group, propylene group, trimethylene group, butylene group, tetramethylene group, pentamethylene group, hexamethylene group, heptamethylene group, octamethylene or the like. R_2 and R_4 are each illustrated by nonamethylene group, decamethylene group, undecamethylene group, dodecamethylene group, tridecamethylene group, tetradecamethylene group, pentadecamethylene group, hexadecamethylene group, cyclohexylene group or the like in addition to the above alkylene groups (except for methylene group). R_5 and R_6 are each concretely exemplified by straight- or branched-chain alkyl groups, such as methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group or tetradecyl group. R_3 and R_8 are each illustrated by a straight- or branched-chain alkyl group, such as a pentadecyl group, in addition to any one of the above alkyl groups.

In the preparation of the refrigerator oils of the present invention, the esters mentioned above may be used singly, or jointly as a mixture of at least two kinds of the esters.

The molecular weight of the ester according to the present invention is not particularly limited, but the number average molecular weight of the ester is in the range of preferably 200-3000, more preferably 300-2000, to improve the compressor in sealability. Further, the kinematic viscosities of the esters according to the present invention are in the range of preferably 2-150 cSt, more preferably 5-100 cSt at 100°C.

A method for producing the esters according to the present invention is not particularly limited. For example, a mixture of the esters can be produced at one time by the esterification reaction of (a) a diol having none of ether linkages in the branched-chains thereof with (b) a dicarboxylic acid and (c) a monocarboxylic acid and/or a monohydric alcohol. The esters are also produced by the reaction of the diol (a) with the monocarboxylic acid (c) or the reaction of the dicarboxylic acid (b) with the monohydric alcohol (c).

The diols (a) used herein are those having 2-16 carbon atoms and are exemplified by alkylene glycols such as ethylene glycol, propylene glycol, butylene glycol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, heptamethylene glycol,

octamethylene glycol, nonamethylene glycol, decamethylene glycol, neopentyl glycol, 2-ethyl-2-methyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 2,4-pentanediol, 2-methyl-2,4-pentanediol, 2-methyl-1,6-hexane, 1,4-cyclohexane dimethanol and 2,2-bis (4-hydroxycyclohexyl) propane.

The dicarboxylic acids (b) used herein are those having 2-10 carbon atoms and are exemplified by saturated aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, methylmalonic acid, ethylmalonic acid, dimethylmalonic acid, methylsuccinic acid, 2,2-dimethylsuccinic acid, 2,3-dimethylsuccinic acid, 2-ethyl-2-methylsuccinic acid, 2-methylglutaric acid, 3-methylglutaric acid, 3,3-dimethylglutaric acid and 3-methyladipic acid; unsaturated aliphatic dicarboxylic acids such as maleic acid, fumaric acid, itaconic acid, citraconic acid and mesaconic acid; and aromatic dicarboxylic acids such as phthalic acid, isophthalic acid and terephthalic acid.

The monocarboxylic acids (c) used herein are those having 2-15 carbon atoms and are exemplified by acetic acid, propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, 3-methylbutanoic

acid, 2-methylbutanoic acid, 2-ethylhexanoic acid, 2,4-dimethylpentanoic acid, 3,3,5-trimethylhexanoic acid and benzoic acid.

The monohydric alcohols (c) used herein are those having 1-15 carbon atoms and are exemplified by methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, unedecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, isopropanol, isobutanol, 2-methyl-1-butanol, 2,2-dimethyl-1-propanol, 3,3-dimethyl-1-butanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2,4,4-trimethyl-1-pentanol, 2,2,4-trimethyl-1-pentanol, 2-ethyl-4-methyl-1-pentanol and 2-ethyl-1-hexanol.

The products obtained by the methods as mentioned above may be refined to remove the by-products and/or unreacted reactants, but the by-products and/or unreacted reactants may be present in small amounts in the refrigerator oils of the present invention as far as they do not impair the excellent performances thereof.

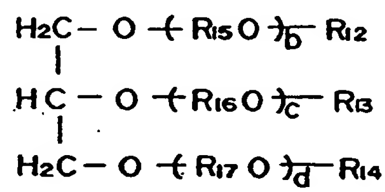
The refrigerator oil of the present invention may comprise as the only base oil the above esters and, as required, it may additionally comprise other base oils for refrigerator oils. Among the other base oils, preferable ones are illustrated as follows:

a polyoxyalkylene glycol or an ether thereof represented by the general formula

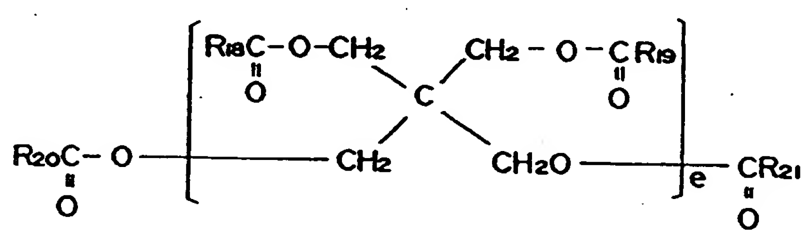
$$R_9 \left(OR_{11} \right)_a OR_{10}$$

wherein R_9 and R_{10} are each a hydrogen atom or an alkyl group having 1-18 carbon atoms, R_{11} is an alkylene group having 2-4 carbon atoms and a is an integer of 5-70,

a polyoxyalkylene glycol glycerol ether represented by the general formula



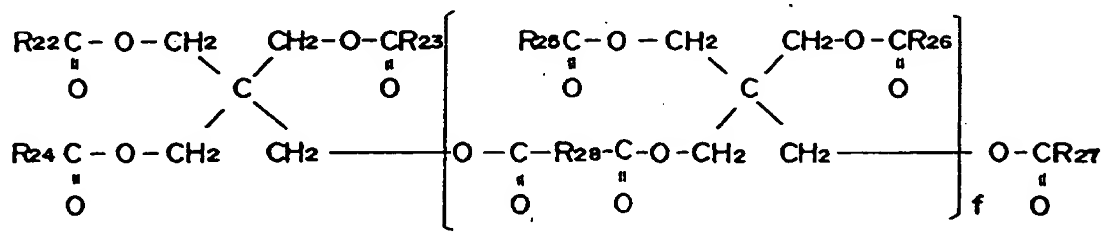
wherein R_{12}-R_{14} are each a hydrogen atom or an alkyl group having 1-18 carbon atoms, R_{15}-R_{17} are each an alkylene group having 2-4 carbon atoms and b-d are each an integer of 5-70, a pentaerythritol ester represented by the general formula



wherein R_{18}-R_{21} may be identical with, or different from, each other and are each a group selected from the group consisting of straight-chain alkyl groups having 3-11 carbon atoms, branched-chain alkyl groups having 3-15 carbon atoms and cycloalkyl groups having 6-12 carbon atoms, the straight-chain alkyl groups being present in a ratio of not

more than 60 % of the total alkyl groups, and e is an integer of 1-3, and

a pentaerythritol dicarboxylic acid ester represented by the general formula



wherein R_{22} - R_{27} are each an alkyl group having 3-15 carbon atoms, R_{28} is a divalent hydrocarbon group having 1-8 carbon atoms and f is an integer of 1-5.

These conventional oils may be used singly or jointly for adding to the refrigerator oil of this invention. Further, the refrigerator oil of this invention may be incorporated with paraffinic mineral oils, naphthenic mineral oils, polyα-olefins, alkylbenzenes and the like, but, in this case, the resulting mixed oil will be lowered in compatibility with chlorine-free type halogenocarbons.

The amount of these conventional base oils so incorporated is not particularly limited as far as the excellent performances of the refrigerator oil of this invention are not impaired, but the esters according to the present invention should be present in the resulting mixed oil in a ratio of usually more than 50 % by weight, preferably not less than 70 % by weight of the total amount of the mixed oil.

The refrigerator oil composition according to this invention may be incorporated further with at least one kind of a phosphorous compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters and phosphorous esters, to improve the oil composition in wear resistance and load resistance. These phosphorous compounds are esters of phosphoric acid or phosphorous acid and an alkanol or a polyether type alcohol, or derivatives of the esters. The phosphoric esters are exemplified by tributyl phosphate, triphenyl phosphate and tricresyl phosphate. The acid phosphoric esters are exemplified by ditetradecyl acid phosphate, dipentadecyl acid phosphate, dihexadecyl acid phosphate, diheptadecyl acid phosphate and dioctadecyl acid phosphate. The amine salts of acid phosphoric esters are exemplified by salts of the above acid phosphoric esters and amines such as methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, triheptylamine and trioctylamine. The chlorinated phosphoric esters are exemplified by tris-dichloropropyl phosphate, tris·chloroethyl phosphate, polyoxyalkylene·bis[di(chloroalkyl)] phosphate and tris·chlorophenyl phosphate. The phosphorous esters are

exemplified by dibutyl phosphite, tributyl phosphite, dipentyl phosphite, tripentyl phosphite, dihexyl phosphite, trihexyl phosphite, diheptyl phosphite, triheptyl phosphite, dioctyl phosphite, trioctyl phosphite, dinonyl phosphite, didecyl phosphite, diundecyl phosphite, triundecyl phosphite, didodecyl phosphite, tridodecyl phosphite, diphenyl phosphite, triphenyl phosphite, dicresyl phosphite, tricresyl phosphite and mixtures thereof. These phosphorous compounds may be added to the refrigerator oil in a ratio of 0.1-5.0 % by weight, preferably 0.2-2.0 % by weight, of the total amount of the refrigerator oil.

To further improve the refrigerator oil of the present invention in stability, it may be incorporated with at least one kind of an epoxy compound selected from the group consisting of phenylglycidyl ether type epoxy compounds, glycidyl ester type epoxy compounds, epoxidized fatty acid monoesters and epoxidized vegetable oils. The said phenylglycidyl ether type epoxy compounds used herein include phenylglycidyl ether and alkylphenylglycidyl ethers. The said alkylphenylglycidyl ethers are those having 1 to 3 alkyl groups having 1 to 13 carbon atoms, among which are preferred those having an alkyl group having 4 to 10 carbon atoms, such as butylphenylglycidyl ether, pentylphenylglycidyl ether, hexylphenylglycidyl ether, heptylphenylglycidyl ether, octylphenylglycidyl ether, nonylphenylglycidyl ether and decylphenylglycidyl ether. The said glycidyl ester type epoxy compounds include

phenylglycidyl esters, alkylglycidyl esters and alkenylglycidyl esters with glycidyl benzoate, glycidyl acrylate, glycidyl methacrylate and the like being preferred.

The epoxidized fatty acid monoesters include esters of an epoxidized fatty acid having 12 to 20 carbon atoms and an alcohol having 1 to 8 carbon atoms, phenol or an alkylphenol. In particular, butyl, hexyl, benzyl, cyclohexyl, methoxyethyl, octyl, phenyl or butylphenyl esters of epoxidized stearic acid may preferably be used.

The epoxidized vegetable oils include epoxidized compounds of vegetable oils such as soybean oil, linseed oil and cottonseed oil.

Among these epoxy compounds, the preferable ones include phenylglycidyl ether type epoxy compounds and epoxidized fatty acid monoesters with the former being more preferable. The most preferred are phenylglycidyl ether, butylphenylglycidyl ether and mixtures thereof.

In a case where these epoxy compounds are to be incorporated in the refrigerator oil of the present invention, it is desirable that they be incorporated therein in a ratio of 0.1-5.0 % by weight, preferably 0.2-2.0 % by weight, of the total amount of the refrigerator oil.

Of course, both of the aforementioned phosphorus compounds and epoxy compounds may be used jointly.

To further enhance the refrigerator oil of this invention in performances, the refrigerator oil may be

incorporated, as required, with heretofore known additives for a refrigerator oil, which include phenol-type antioxidants such as di-tert.-butyl-p-cresol and bisphenol A; amine-type antioxidants such as phenyl-α-naphthylamine and N,N-di(2-naphthyl)-p-phenylenediamine; wear resistant additives such as zinc dithiophosphate; extreme pressure agents such as chlorinated paraffin and sulfur compounds; oiliness improvers such as fatty acids; antifoaming agents such as silicone-type ones; and metal inactivators such as benzotriazole. These additives may be used singly or jointly. The total amount of these additives added is ordinarily not more than 10 % by weight, preferably not more than 5 % by weight, of the total amount of the refrigerator oil.

The refrigerator oils of this invention comprising the esters as the base oil should have such viscosity and pour point as those which are normally suitable for an ordinary refrigerator oil, but they should desirably have a pour point of not higher than -10°C, preferably -20°C to -80°C, to prevent them from solidification at a low temperature. Further, they should desirably have a kinematic viscosity of not less than 2cSt, preferably not less than 3cSt at 100°C, to keep the sealability of the compressor when used, while they should desirably have a kinematic viscosity of not more than 150cSt, preferably not more than 100cSt at 100°C, in veiw of their fluidity at a

low temperature and the efficiency of heat exchange in the evaporator when used.

The refrigerator oils of the present invention are very excellent in compatibility with the chlorine-free type halogenocarbons as compared with the heretofore known refrigerator oils. The chlorine-free type halogenocarbons are exemplified by 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1-difluoroethane (HFC-152a) and trifluoromethane (HFC-23), with HFC-134a being preferred.

Further, the refrigerator oils of the present invention are excellent ones which have not only high compatibility with the chlorine-free type halogenocarbons and high electrical insulating property but also high lubricity and low hygroscopicity.

The refrigerator oils of the present invention may particularly preferably be used in refrigerators, air-conditioners, dehumidifiers, cold-storage chests, freezers, freeze and refrigeration warehouses, automatic vending machines, showcases, cooling units in chemical plants, and the like which have a reciprocating or rotary compressor. Further, the above refrigerator oils may also preferably be used in refrigerators having a centrifugal compressor.

[Examples]

This invention will be better understood by the following Examples and Comparative Examples.

Examples 1-7 and Comparative Examples 1-6

Refrigerator oils of this invention and comparative refrigerator oils of a conventional type are illustrated as follows:

[Example 1] A diester of adipic acid and 2-ethyl-1-hexanol:

$$R_1\text{-}O\text{-}CO\text{-}(CH_2)_4\text{-}COO\text{-}R_1 \qquad R_1\ ;\ \text{-}CH_2\text{-}\underset{\substack{|\\ C_2H_5}}{CH}\text{-}(CH_2)_3\text{-}CH_3$$

[Example 2] A diester of 3-methyl-1,5-pentanediol and 3,5,5-trimethylhexanoic acid:

$$R_2\text{-}COO\text{-}C_2H_4\text{-}\underset{\substack{|\\ CH_3}}{CH}\text{-}C_2H_4\text{-}O\text{-}CO\text{-}R_2 \qquad R_2\ ;\ \text{-}CH_2\text{-}\overset{\substack{CH_3\\ |}}{CH}\text{-}CH\text{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}\text{-}CH_3$$

[Example 3] A complex ester having an average molecular weight of about 500 of 3-methyl-1,5-pentanediol, adipic acid and 3,5,5-trimethylhexanoic acid:

$$R_2\text{-}COO\text{-}C_2H_4\text{-}\underset{\substack{|\\ CH_3}}{CH}\text{-}C_2H_4\text{-}O\text{-}CO\text{-}R_2$$

and

$$R_2\text{-}COO\text{-}C_2H_4\text{-}\underset{\substack{|\\ CH_3}}{CH}\text{-}C_2H_4\text{-}O\left[CO\text{-}(CH_2)_4\text{-}COO\text{-}C_2H_4\text{-}\underset{\substack{|\\ CH_3}}{CH}\text{-}C_2H_4\text{-}O\right]_n CO\text{-}R_2 \qquad n \geqq 1$$

[Example 4] A complex ester having the same composition as that in Example 3 except for having an average molecular weight of about 700

[Example 5] A complex ester having an average molecular weight of about 520 of 3-methyl-1,5-pentanediol, adipic acid and 2-ethyl-1-hexanol:

$$R_1-O-CO-(CH_2)_4-COO-R_1$$

and

$$R_1-O\left[CO-(CH_2)_4-COO-C_2H_4-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_2H_4-O\right]_n CO-(CH_2)_4-COO-R_1 \qquad n\geqq 1$$

[Example 6] A complex ester having the same composition as that in Example 5 except for having an average molecular weight of about 750

[Example 7] A mixture of the same complex ester as in Example 3 and 1.0 wt.% of a phosphoic ester type wear inhibitor

[Comparative Example 1] A naphthenic mineral oil

[Comparative Example 2] A branched-chain type alkylbenzene (average molecular weight: about 300)

[Comparative Example 3] Polyoxypropylene glycol monobutyl ether (average molecular weight: about 500)

[Comparative Example 4] Polyoxypropylene glycol monobutyl ether (average molecular weight: about 1000)

[Comparative Example 5] Polyoxypropylene glycol (average molecular weight: about 700)

[Comparative Example 6] Polyoxypropylene glycol (average molecular weight: about 2000)

The base oils of Examples 1-7 for the refrigerator oils of the present invention were evaluated for their performances that are their compatibility with HFC-134a, insulating property, wear resistance and hygroscopicity by the following respective test methods. For comparison, the mineral oil, the alkylbenzene, the polypropylene glycol monoalkyl ethers and the polyalkylene glycols disclosed in U.S. Patent No. 4,755,316 of the Comparative Examples which have heretofore been used as refrigerator oils were evaluated in the same manner as in Examples 1-7. The results are indicated in Table 1.

(Miscibility with HFC-134a)

0.2 g of the test oil of each of the Examples and the Comparative Examples and 1 g of the refrigerant (HFC-134a)

were sealed in a glass tube having an inner diameter of 6 mm and a length of 220 mm. This glass tube was then placed in a thermostat maintained at a predetermined low temperature or high temperature to observe whether the refrigerant and the test oil were miscible with each other, separated from each other or made white-turbid.

(Insulating property)

The test oils were each measured for specific volume resistivity at 25°C in accordance with JIS C 2101.

(FALEX wear test)

The test oils were each applied to a test journal for measuring the amount of the test journal worn by having the journal run in at a test oil temperature of 100 °C under a load of 150 lb for 1 minute and then running it under a load of 250 lb for 2 hours in accordance with ASTM D 2670.

(Hygroscopicity)

Thirty grams (30 g) of each of the test oils were placed in a 300-ml beaker, allowed to stand for 7 days in an air-conditioned bath maintained at a temperature of 60 °C and a humidity of 30 % and then measured for water content by the Karl-Fischer method.

Table 1

Example Comparative Example	Kinematic viscosity @ 100°C (cSt)	Miscibility with HFC-134a Miscible temperature range (°C)	Resistivity @25°C (Ω·cm)	FALEX test Amount of journal worn (mg)	Hygroscopicity 60°C,30% (%)
Example1	2.3	-24 - CT *	4.2×10^{14}	24	0.22
Example2	3.1	-30 - CT	3.9×10^{14}	22	0.20
Example3	5.5	-55 - CT	2.5×10^{14}	15	0.18
Example4	10.3	-34 - 95	1.4×10^{14}	12	0.11
Example5	6.2	-47 - CT	2.2×10^{14}	14	0.16
Example6	11.6	-30 - 92	1.1×10^{14}	10	0.10
Example7	5.5	-55 - CT	2.3×10^{14}	2	0.18
Com.Ex.1	5.1	Immiscible	-	-	-
Com.Ex.2	4.8	Immiscible	-	-	-
Com.Ex.3	4.9	<-70 - 97	1.1×10^{11}	40	1.31
Com.Ex.4	10.8	<-70 - 56	1.2×10^{11}	35	1.01
Com.Ex.5	10.6	<-70 - 64	5.6×10^{10}	38	2.30
Com.Ex.6	22.4	-51 - 32	4.8×10^{10}	30	1.81

*: CT; Critical temperature of HFC-134a (102°C)

It is apparent from the results indicated in Table 1 that the refrigerator oils (Examples 1-7) of the present invention are very excellent in miscibility with a refrigerant, HFC-134a, as compared with those of Comparative Examples 1-2.

The polyalkylene glycols of Comparative Examples 3-6 are excellent in miscibility with the refrigerant, but these glycols are inferior in insulating property thereby rendering them unusable for hermetic type compressors.

The FALEX wear test shows that the refrigerator oils of Examples 1-7 are at least equal in wear resistance to those of Comparative Examples 3 and 6.

Further, the refrigerator oils of Examples 1-7 have lower hygroscopicity than the alkylene glycols of Comparative Examples 3-6, that is, the refrigerator oils are excellent in hygroscopicity.

[Effect of the Invention]

As is apparent from the above comparative experiments, lubricating oils for compressors of refrigerators of the present invention are suitable for use in refrigerators using therein a chlorine-free type halogenocarbon as a refrigerant and are excellent in electrical insulating property as well as wear resistance and nonhygroscopicity.